

A Water Blown Urethane Insulation for Use in Cryogenic Environments

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Abstract

Thermal Protection Systems (TPS) of NASA's Space Shuttle External Tank include polyurethane and polyisocyanurate modified polyurethane foam insulations. These insulations, currently foamed with CFC 11 blowing agent, serve to maintain cryogenic propellant quality, maintain the external tank structural temperature limits, and minimize the formation of ice and frost that could potentially damage the ceramic insulation on the space shuttle orbiter. During flight the external tank insulations are exposed to mechanical, thermal and acoustical stresses. TPS must pass cryogenic flexure and substrate adhesion tests at -253°C, aerothermal and radiant heating tests at fluxes up to approximately 14 kilowatts per square meter, and thermal conductivity tests at cryogenic and elevated temperatures.

Due to environmental concerns, the polyurethane insulation industry and the External Tank Project are tasked with replacing CFC 11. The flight qualification of foam insulations employing HCFC 141b as a foaming agent is currently in progress; HCFC 141b blown insulations are scheduled for production implementation in 1995. Realizing that the second generation HCFC blowing agents are an interim solution, the evaluation of third generation blowing agents with zero ozone depletion potential is underway. NASA's TPS Materials Research Laboratory is evaluating third generation blowing agents in cryogenic insulations for the External Tank; one option being investigated is the use of water as a foaming agent. A dimensionally stable insulation with low friability, good adhesion to cryogenic substrates, and acceptable thermal conductivity has been developed with low viscosity materials that are easily processed in molding applications. The development criteria, statistical experimental approach, and resulting foam properties will be presented.

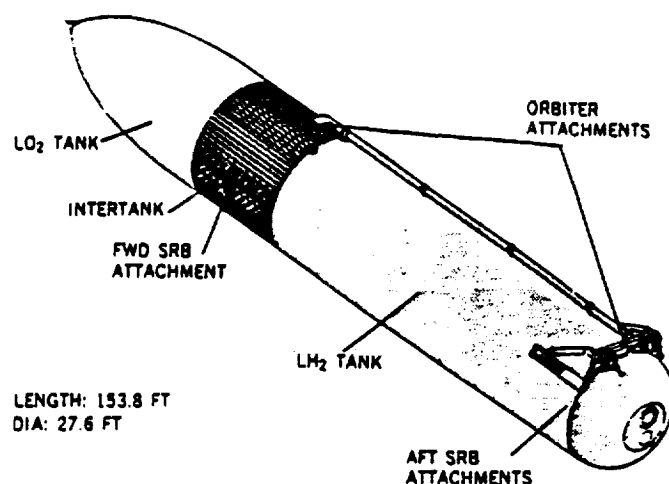
Introduction

The purpose of this study was to evaluate the use of water blown polyurethane based insulations in cryogenic environments. Success criteria included the following insulation properties: low friability, good adhesion, cryogenic strain compatibility, dimensional stability, high closed cell content, and acceptable thermal conductivity. Emphasis was placed on adhesion to an epoxy primed aluminum substrate and on flexibility at cryogenic temperatures.

External Tank Insulations

The External Tank serves as a cryogenic propellant tank and also as a structural backbone for the Space Shuttle system. Figure 1 shows the main components of the External Tank; they are a forward liquid oxygen tank, an intertank, and the aft liquid hydrogen tank. Thermal Protection Systems (TPS) of the External Tank include high density silicon based ablative resins, polyisocyanurate spray on foam insulations, and both sprayable and moldable polyurethane insulations. The TPS serves to prevent the formation of ice and frost on the tank surface, maintain structural temperature limits, and maintain propellant quality. The polyurethane pour foam was selected as the first target application for the water blown insulation.

Figure 1. External Tank Structure



Industry Studies

Over the past few years, several papers have been presented on the development of rigid foams blown with carbon dioxide from the water-isocyanate reaction. The industry has found this technically challenging and economically inviting. Issues associated with these water blown foams include: increased thermal conductivity, high open cell content, accelerated foam aging, poor dimensional stability, high friability, and poor adhesion [1,2]. The primary concern lies with the high diffusion rates of carbon dioxide in the polymer matrix of the foam. The rapid diffusion of carbon dioxide out and the slower ingress of air components leads to foam shrinkage and higher thermal conductivities [3,4]. The thermal conductivities of these gases are presented in Table 1. Processing of water blown foams is more difficult because of the inherently higher viscosities of the polyol components. Several have found that molding of these foams is complicated by poor flowability and high molding pressures [5-7]. Nevertheless, systems have been developed for use in appliances, vending machines, water heaters, supermarket display cases, and picnic coolers.

Gas	K (BTU.in/ft ² .h.°F)
Nitrogen	0.168
Air	0.168
Oxygen	0.170
Carbon Dioxide	0.102
Trichlorofluoromethane	0.068

Experimental

Developmental Approach

The polymer structure was modified to incorporate higher molecular weight polyols that could compensate for the high crosslink density associated with water blown foams without sacrificing dimensional stability. The experimental sequence was initiated by screening several polyols for their effect on foam friability, substrate adhesion, and closed cell content. The polyols evaluated are presented in Table 2. Six polyols were then selected for further study. A statistically based experiment was designed to evaluate these polyols and determine the optimum ratio required to achieve a dimensionally stable foam with cryogenic compatibility. Thirty foam formulations were blended, foamed, and tested with varying levels of each of the six polyols. Three replicate formulations were included in the experiment to allow estimation of the replicate standard deviation of the foam properties. In each of the

experimental formulations, isocyanate index was held constant at 150, while surfactant and water levels were held constant at 2 and 1.25% of the total formulation respectively. Data was analyzed and fitted with quadratic models. These empirically based models were then used to evaluate the trade-offs in material properties associated with various polyol ratios.

Table 2. Polyols Evaluated

Polyol #	OH Equivalent Weight
1	246
2	180
3	170
4	119
5	156
6	167
7	200
8	106
9	94
10	330

Foam Preparation

Foams were prepared by preblending the polyol component, and then combining stoichiometric weights of polyol and polymeric isocyanate for mixing. The room temperature liquid components were hand mixed for 8 seconds at 12,000 rpm with a Premier Mill Laboratory Dispersator. The reacting mixture was then poured into paper cups for manual reactivity measurement, or separately into a Timetech reactivity unit for automatic data acquisition of foam exotherm temperature, foam gelation pressure, and foam rise height. The catalyst levels for each of the thirty formulations was adjusted to maintain a constant reactivity for all systems.

Initial polyol screening tests were conducted with room temperature, free rise box pours. Test panels for the polyol optimization experiment were made in 10"x20"x3" molds. Four room temperature molds containing an epoxy primed aluminum substrate were poured for each of the thirty formulations. Panels were cured a minimum of one hour at room temperature before demolding. An additional 2 week aging period was allowed before test samples were cut and prepared from the panels.

Foam Properties

Table 3 lists the tests conducted on the foam insulations. Emphasis was placed on the results of the adhesion and cryogenic flexure tests. Bond tensile samples were tested at -196°, 21°, and 93°C to measure substrate adhesion. Four point flexure samples were tested at -196°C. Tensile and flexure tests are currently being run at -253°C.

Table 3. Test Methods

Foam Property	Method	Units
Bond Adhesion (1)	ASTM D 1623	psi
Compression	ASTM D 1621	psi
Density	ASTM D 1622	pcf
Friability	ASTM C 421	%mass loss
Closed Cell Content	ASTM D 2856	% closed cells
Thermal Conductivity	ASTM C 177	BTU.in/ft ² .h.°F
Oxygen Index	ASTM D 2863	%oxygen
4-Point Flexure	In-House Test	psi

Note: (1) Adhesion to epoxy primed 2219 aluminum alloy

Results

The results of the polyol screening tests are presented in Table 4. The results show a broad range of foam properties with bond tension values ranging from 20 to over 100 psi in room temperature tests. Elongation measured in the bond tension tests was used as an indicator of four point flexibility. Based on

these test results, Polyols 1 through 6 were selected for further study. Table 5 presents the levels at which the polyols were evaluated in the experiment.

Table 4. Results of Polyol Screening

Polyol #	21°C Bond Tension	% Elongation	Compression	% Closed Cells	Friability	Oxygen Index
1	20	18	5	80.7	3.84	21.0
2	79	10	31	91.5	1.34	20.9
3	79	9	31	92.2	0.38	20.8
4	107	11	34	92.6	1.45	21.0
5	78	10	48	93.8	0.39	19.8
6	44	9	33	93.2	1.37	20.9
7	64	9	27	92.2	0.23	20.5
8	38	8	41	93.1	1.27	21.0

Table 5. Experimental Variables

Variable	Range
Polyol 1	0 to 30 % of Polyol Blend
Polyol 2	0 to 100% of Polyol Blend
Polyol 3	0 to 100% of Polyol Blend
Polyol 4	0 to 100% of Polyol Blend
Polyol 5	0 to 100% of Polyol Blend
Polyol 6	0 to 100% of Polyol Blend

The thirty formulations evaluated in this experiment had the following constant variables: isocyanate index of 150, common surfactant, and 1.25% water in the total formulation. Material properties varied considerably with the change in polyols. Several of the test panels debonded from the aluminum substrate with demolding, while others had good substrate adhesion.

Results of the mechanical and physical testing were reduced and analyzed with Echip™ software to determine the effects of the various polyol ratios on foam properties. The R-square values, indicating how well the empirical models fit the experimental data, are presented in Table 6. Polyol 1 was found to have the greatest effect on the foam flow in the molds, and based on the empirical models also contributed to cryogenic bond tensile strength and four point flexibility. Polyols 3 and 6 contributed to dimensional stability and improved oxygen index. The optimum formulation having the best combination of properties, substrate adhesion greater than 50 psi and cryogenic flexibility, was obtained with the polyol blend consisting of 20% Polyol 1, 50% Polyol 3 and 30% Polyol 6.

Table 6. Degree of Fit of Empirical Models

Property Modeled	R-square value
Bond Tension, 21°C	0.827
Bond Tension, 93°C	0.741
Bond Tension, -196°C	0.861
4-point Flexure, Stress at failure	0.814
4-point Flexure, Strain at failure	0.878

Figures 2 to 4 are two dimensional contour plots illustrating the effects of polyol ratio on substrate adhesion at various temperatures. These plots show the detrimental effects of Polyol 1 when used at levels greater than 30% of the polyol blend. Figures 5 and 6 show the maximum stress and strain in a four point flexure test are obtained with Polyol 1 added at approximately 25% of the polyol blend.

An evaluation of a phosphorous based flame retardant in the water blown foam was conducted. Table 7 presents the effects of the non-reactive flame retardant on the foam properties of gel time, density, and oxygen index. The flame retardant was added to the foam system at levels ranging from zero to twenty-five percent of the total formulation. Based on this limited data, a flame retardant level of 12% was selected.

Table 7. Effects of Added Flame Retardant

% FR	Gel (sec)	Density	Oxygen Index
0	43	2.5	<20.9
4	52	2.5	23.0
7	53	2.5	24.0
10	56	2.5	25.0
15	57	2.5	26.1
20	58	2.6	26.9
25	62	2.8	27.3

These oxygen index values are not intended to reflect hazards presented by this or any other material under actual fire conditions.

As a result of this study, a water blown molding insulation has been developed with acceptable mechanical properties at cryogenic temperatures. Table 8 presents data for this insulation, System A, and a comparable insulation, System B, that is co-blown with CFC 11 and water. The reaction profile of System A is illustrated in Figure 7 which shows the rise in foam exotherm temperature with time.

Table 8. Properties of the Water Blown Insulation

Foam Property	System A Water Blown	System B Control (1)
Density		
Free Rise	2.3	2.5
Molded	2.6	3.0
Bond Adhesion (2)		
-196°C	63	38
21°C	83	64
93°C	49	33
Compression	28	30
Friability	1	26
Closed Cell Content	93	87
Thermal Conductivity	0.20	0.17
Oxygen Index	25	23

Note:

1. CFC 11 and water co-blown
2. Adhesion to epoxy primed 2219 aluminum alloy

Conclusions

The development of a water blown insulation for use in cryogenic environments required the development of a polymer network with reduced crosslink density to obtain a low friability insulation with good adhesion to epoxy primed aluminum substrates. This development work completed with a molding system will serve as a platform for further development of a sprayable, water blown foam insulation. Statistically designed experiments have been employed in the evaluation of a catalyst package for accelerated reactivity suitable in spray formulations, and are currently being used in a processing sensitivity study to evaluate the parameters of substrate temperature, relative humidity, and component temperature on foam properties. As industry continues to develop low viscosity and low permeability polyols, improved surfactants and catalysts, the use of rigid water blown foams in a variety of applications will grow.

Acknowledgments

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